

CHAPTER III EXPERIMENTAL

3.1 Materials and Apparatus

3.1.1 Chemicals and Materials

- Polypropylene homopolymer (PP 1102K) pellets with MFI of 4 g/10 min (190 °C, 2.16 kg), IRPC Co. Ltd., Thailand.
- Organoclay prepared in our laboratory by using sodium activated bentonite (kindly supplied by Thai Nippon Co., Ltd., Thailand) and distearoylethyl hydroxyethylmonium methosulfate and cetearyl alcohol.
- Sodium-neutralized ethylene-co-methacrylic acid, Surlyn[®]PC350 (Dupont), MFI of 4.5 g/10 min (190 °C, 2.16 kg), Dupont[™], USA.
- Copper (II) nitrate, Ajax Finechem Pty Ltd., analytical grade
- Polyvinylpyrrolidone (PVP, MW 40000), Sigma-Aldrich, Germany.
- L-ascorbic acid, Ajax Finechem Pty Ltd., laboratory grade
- Ethylene vinyl acetate (EVA), Dupont
- Fresh mangosteen (*Garcinia mangostana* Linn.)
- Distilled water

3.1.2 Apparatus and Glass Wares

- Round bottom flask 250 ml
- Glass condenser
- Erlenmeyer flask 250, 500 ml
- Beaker 25, 50, 250, 500 ml
- Cylinder 100 ml
- Glass stirrer
- Magnetic stirrer
- Spatulas

- Glass droplets
- Desiccators
- Thermostat heater
- Vacuum oven
- Analytical balance
- Centrifugal unit and centrifugal tube
- pH meter (CyberScan pH1000)

3.2 Equipment

- 3.2.1 Haake Rheomex PTW-16 co-rotating twin-screw extruder with $D = 16$ mm and $L/D = 25$.
- 3.2.2 Blown film extruder (PP50, Thailand).
- 3.2.3 Hot pressing machine (PR1D-W300L350, Chareon Tut, Thailand).
- 3.2.4 Transmission emission spectrophotometer (TEM, JEOL JEM-2100 model).
- 3.2.5 X-ray Diffraction Microscope (XRD) (Bruker AXS Model D8).
- 3.2.6 Scanning Electron Microscope (SEM) (JEOL JEM 5800 LV).
- 3.2.7 Universal testing machine (Instron 5969, Instron Engineering Corp., USA).
- 3.2.8 Differential Scanning Calorimeter (Mettler DSC 1, Mettler Toledo, Switzerland).
- 3.2.9 Thermogravimetric analysis (Mettler TGA, Mettler Toledo, Switzerland).
- 3.2.10 UV-VIS-NIR spectrophotometer (Perkin-Elmer Lambda900) in transmittance mode.
- 3.2.11 Chroma meter (HunterLab Model Colorflex with $4^{50/00}$ optical geometry and EasyMatch® QC software).
- 3.2.12 Vapor Permeation Tester (Model L80-4000, LYSSY).
- 3.2.13 Oxygen Permeation Analyzer Model 8000, Illinois Instrument Inc.

3.3 Experimental

3.3.1 Synthesis of Copper Nanoparticle (CuNP)

Copper nanoparticles (CuNP) were prepared with a fixed ratio of chemicals in order to produce the same particle size distribution as discussed in Wu *et al.* (2006). 50 ml aqueous solution of 0.4 M L-ascorbic acid and 0.8 M polyvinylpyrrolidone (PVP) were directly mixed with another 50 ml aqueous solution of 0.01 M copper (II) nitrate and 0.8 M PVP under stirring. Then, the mixture was kept at 45 °C without any inert gas protection. After about 1 hour, the initial precursor solution with light blue color changed red colloidal slurry, indicating the formation of CuNPs. The reaction was kept for 3 hours to complete reduction reaction of copper (II) ion into copper (0) nanoparticles. The colloidal slurry was kept to mix with organoclay in the next step.

3.3.2 Mixing of CuNP into Bentonite Organoclay (OBEN/CuNP)

Bentonite organoclay (OBEN) was dispersed and allowed them to swell in distilled water for 12 hours. Then, the synthesized copper colloidal slurry was added into swollen organoclay slurry with vigorous stirring to allow good distribution between them for 20 min. The weight of CuNP adding into organoclay was calculated to vary nominal contents of 0, 5, 10, 15, and 20 wt%. The abbreviation for OBEN-CuNP mixture is denoted as OBEN-CuNP_x, where x is the amount of copper nanoparticle content (0, 5, 10, 15, and 20 wt%) in the powder mixture.

The OBEN-CuNP_x mixture was allowed to sediment for 12 hours. Removal of excess PVP solution was performed by pouring out water above the sediment and adding fresh distilled water into suspended mixtures until clear water was observed above the sediment. The sediment was dried in a vacuum oven at 80°C for 24 hours, and then grinded by hand to produce fine powder.

3.3.3 Nanoparticle Characterization

Transmission electron microscopy (TEM) of synthesized copper nanoparticles was performed on JEOL JEM-2100 model and an accelerating voltage of 150 kV. Samples for the TEM imaging were prepared by placing a drop of the

colloidal solution on a copper grid. Particle size distribution of synthesized copper nanoparticles was also determined by a particle size analyzer (Malvern Instrument).

Powder X-ray diffraction patterns were measured on a Bruker AXS Model D8 diffractometer with CuK_α radiation operate at 40 kV and 30 mA. The OBEN/CuNP powder was observed on the 2θ range of 2-80 degree with a scan speed of 2 degree/min and scan step of 0.01 degree.

3.3.4 Preparation of OBEN/CuNP Masterbatch

The masterbatch of OBEN/CuNP was prepared by mixing dried OBEN/CuNP mixture with Surlyn® P350 in a ratio of 1:2 by weight, in a Haake Rheomex PTW-16 co-rotating twin-screw extruder with $D = 16$ mm and $L/D = 25$. The operating temperature of extruder was set at 180 °C with a screw speed of 70 rpm. Extrudate was pelletized for further mixed with PP pellets in a ratio of PP:OBEN/CuNP_x = 99:1 wt%. The letter x refers to copper nanoparticle content in wt% adding into OBEN-CuNP mixture.

3.3.5 Preparation of Neat PP and PP Nanocomposite Films

Neat PP, PP/Surlyn, PP/OBEN, and PP/OBEN-CuNP_x film samples were fabricated using a water-quenched blown film extruder (PP50, Thailand). Temperature profiles were 210, 220, 220, and 210 °C from feed zone to die. Screw speed was kept constant at 80 rpm. Bubble forming ring of 23 cm in water bath was used, which final width of blown film was about 22-23 cm. Nip-roll speed and pull-out speed were adjusted to produce blown films with final thickness of 40-50 μm . Table 3.1 summaries the abbreviations of the blown film samples and their compositions after mixing the masterbatch with neat PP.

3.3.6 Clarity and Mechanical Properties of Neat PP and PP Nanocomposite Films

Clarity and color of film samples was determined using a UV-VIS-NIR spectrophotometer (Perkin Elmer Lambda 900) in transmittance mode. Lightness (L^*) and color in Lab system was reported.

Table 3.1 Abbreviations and composition of blown films

Abbreviations	PP (wt%)	Bentonite organoclay (wt%)	CuNP (wt%)	Surlyn (phr)
Neat PP	100.0	-	-	-
PP/Surlyn	100.0	-	-	2
PP/OBEN	99.0	1.00	-	2
PP/OBEN-Cu5	99.0	0.95	0.05	2
PP/OBEN-Cu10	99.0	0.90	0.10	2
PP/OBEN-Cu15	99.0	0.85	0.15	2
PP/OBEN-Cu20	99.0	0.80	0.20	2

Tensile strength and elongation at break of neat PP and PP nanocomposite films were measured in accordance to ASTM D-882 using a universal testing machine (Instron 5969, Instron Engineering Corp., USA). Using a sharp razor blade, film specimens were cut from blown films in machine and transverse directions to obtain rectangular strips of 25.4 mm x 127 mm long. Gauge length of 50 mm was used, and crosshead speed was set at 50 mm/min. Before testing, thickness of film specimens was measured along the length in 5 different areas to determine average thickness. Ten specimens in machine and transverse directions were tested, and five data with closed standard deviation was selected to represent the average and standard deviation.

Tear propagation resistance of neat PP and PP nanocomposite films were measured in accordance to ASTM D-1938 using a universal testing machine (Instron 5969, Instron Engineering Corp., USA). Using a sharp razor blade, film specimens were cut from blown films in machine and transverse directions to obtain rectangular strips of 25 mm x 76 mm long. Before testing, thickness of film specimens was measured along the length in 5 different areas to determine average thickness. The grip-separation speed was set at 250 mm/min. The load necessary to propagate the tear through the entire unslit 25 mm portion was recorded. Ten specimens in machine and transverse directions were tested, and five data with

closed standard deviation was selected to represent the average and standard deviation.

3.3.7 Morphology of Neat PP and PP Nanocomposite Films

Dispersion of nanoparticles (OBEN and OBEN-CuNP) in PP matrix and compatibility of the PP/Surlyn/OBEN-CuNP tertiary phases were carried out using SEM (JEOL JEM 5800 LV). Film samples were dipped and fractured in liquid nitrogen. Then the samples were sputtered with gold before viewing under scanning electron microscope (SEM) operating.

Nanoscale dispersion of nanoparticles (OBEN and OBEN-CuNP) in PP matrix was studied using XRD (Bruker AXS Model D8) diffractometer with CuK_α radiation operate at 40 kV and 30 mA. The film samples were observed on the 2θ range of 2-10 degree with a scan speed of 2 degree/min and scan step of 0.01 degree.

3.3.8 Thermal Properties of Neat PP and PP Nanocomposite Film

Crystallinity and melting behaviors of neat PP and PP nanocomposite films were studied with a Differential Scanning Calorimeter (Mettler DSC 1, Mettler Toledo, Switzerland). All operations were performed under a nitrogen atmosphere. The samples were first heated from 25 °C to 250 °C at the heating rate of 10 °C/min in order to eliminate the influence of thermal history and then cooled down at rate of 10 °C/min from 250 °C to 25 °C to observe the melt crystallization behavior. The samples were then reheated to 250 °C at the same rate.

Thermogravimetric analysis (TGA) was used to study thermal stability of neat PP and PP nanocomposite films. TG-DTA curves were collected on a METTLER TG/DTA instrument. The degradation temperature, initial degradation temperature, weight loss and final degradation temperature of the samples were determined. The samples were loaded on ceramic pan and heated from 25°C to 800°C at heating rate 10°C/min and flow under nitrogen gas of 200 ml/min.

3.3.9 Permeability of Neat PP and PP Nanocomposite Films

Vapor Permeation Tester Model L80-4000, LYSSY was used to determine water vapor permeability of neat PP and PP nanocomposite blown films. Water vapor permeation experiments were investigated following procedure

described in ASTM E398. The test was performed at 38°C with water vapor pressure of 49.7 mmHg. The blown films were cut into circular shape with 15 cm in diameter. The thickness of films was measured using the peacock digital thickness gauge model PDN 12N by reading 15 points at random position over test area.

Oxygen Permeation Analyzer Model 8000, Illinois Instrument Inc., was used to determine oxygen permeability of neat PP and PP nanocomposite blown films. Gas permeation experiments were investigated following procedure described in ASTM D3985. The test was carried out at 23°C with oxygen flow rate of 40 cm²/min. The blown films were cut into circular shape with 15 cm in diameter. The thickness of films was measured by using the peacock digital thickness gauge model PDN 12N by reading 15 points at random position over test area.

3.3.10 Antimicrobial Activity of Neat PP and PP Nanocomposite Films

Bacterial sensitivity to antibiotics was carried out using the agar diffusion test. Prior to mixing, sample powder and distilled water were autoclaved at 120 °C. Paste of OBEN and OBEN-CuNP were prepared by mixing 0.2 gram of sample powder in 50 µl distilled water. The Escherichia coli (E.coli) suspension (100 µl of 10⁴ – 10⁵ CFU ml⁻¹) was applied uniformly on the surface of nutrient agar plate, and then five holes were cut on the agar plate for placing the powder paste. Distilled water was put into the center hole as the control reference. Each sample (OBEN, OBEN-CuNP5, OBEN-CuNP10, OBEN-CuNP15, and OBEN-CuNP20) were put into two holes in the plates. The plates were incubated at 35 °C for 24 h, after which photo of the inhibition zone (clear zone) surrounding the paste was taken for comparison. The same procedure was also performed using small pieces of neat PP and PP composite blown films as the antibiotics.